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S. Karpushenkov[1], M. Serdechnova[2], M. Mohedano[3],
L. Karpushenkava[1], C. Blawert[2], M. Zheludkevich[2]
1. Belarusian State University, Faculty of Chemistry,
4, Nezavisimosti avenue, 220030, Minsk, Belarus
2. Magnesium Innovation Center, Helmholtz-Zentrum Geesthacht, Max-Plank-Straβe 1,
21502 Geesthacht, Germany
3. Departamento de Ciencia de Materiales, Facultad de Ciencias Químicas, Universidad
Complutense, 28040 Madrid, Spain

SYNTHESIS OF ACTIVE PROTECTIVE PEO-LDH COATINGSON AA2024 ALLOY

Recently, layered double hydroxides (LDHs) have been extensively investigated as environmentally friendly nanocontainers useful for active anticorrosion protection of metallic substrates. They are promising to be used replace chromates, whicht are banned in many industries because of a high toxicity. Being loaded with corrosion inhibitors, LDHs act as "smart" nanocontainers: the release of corrosion inhibitor and the formation of protective layer happen only when defects occur and corrosion starts [1]. One of the problem, which takes place when LDHs are directly grown on the surface of bare metal, is their fragility. In order to overcome this disadvantage, it was suggested recently to grow LDH [2-3] on the PEO (plasma electrolytic oxidation) treated surfaces in order to combine barrier protection provided by PEO layer with self-healing protection, provided by LDHs.

PEO is an environmentally friendly technique, based on anodizing process, leading to the formation of ceramic-like coatings under highvoltage discharges. Being hard and well-adherent to the substrate, PEO layers improve both corrosion and wear resistance of the material. Unfortunately, the electrical discharges and high stresses in the layer create discharge channels, pores from gas inclusions and cracks in the coating [4].

Direct synthesis of LDH structures on the surface and inside pores of PEO treated aluminum alloy and their loading with corrosion inhibitors opens a lot of new opportunities to increase the active protection of alloys and allows to keep the protective properties of PEO for longer time.

Synthesis of active protective PEO-LDH coatings on the surface AA2024 and their loading with corrosion inhibitor was carried out in 3 steps: synthesis of PEO coatings; synthesis of Zn-Al-LDH-NO_3 structures on the and in pores of PEO coating; and inhibitor intercalation [2].

The PEO processing of AA2024 alloy was conducted at constant voltage using four different sets of conditions (350 V, 400 V, 450 V, 500 V)

and three different times 5, 15 and 30 min. A pulsed DC power supply with a pulse ratio of 1 to 9 ms (t_{on}:t_{off}) was used. Silicate-phosphate based electrolyte (9 g L^{-1} Na_2SiO_3, 2 g L^{-1} NaOH and 11 g L^{-1} $Na_2H_2P_2O_7$) was used in this work [3]. Depending on the oxidation time and the voltage value, the coating thickness was from 1 to 13 μm. Prior to the PEO processing, specimens were etched in NaOH solution (20 wt. %), rinsed in deionized water, desmutted in HNO_3 solution (65 wt.%), rinsed in deionized water again and, finally, dried under air conditions.

For direct synthesis of Zn-Al-LDH-NO_3 structures on the surface and inside pores of PEO covered aluminum alloy using zinc nitrate and ammonium nitrate were dissolved in deionized water (pH of solution was adjusted to 6.5 by slow adding of 1 % ammonia under continuous stirring). The specimens were immersed in the solution at 95 ^{O}C for 30 minutes under continuous stirring then rinsed in deionized water and dried in air at a room temperature (product of this treatment is called PEO-LDH-NO_3).

The inhibitor loading was performed as a result of anion exchange reaction between the nitrate from LDH galleries (prepared on the surface of PEO coating) and vanadate from 0.1M $NaVO_3$ solution (the reaction was carried out for 30 min at 50 °C, pH adjustment to 8.4 using 1M NaOH solution). The product of anionic-exchange reaction between PEO-LDHNO_3 structure and $NaVO_3$ solution is called PEO-LDH-VO_x (in frame of this work). After the anion exchange reaction, the specimens were rinsed with deionized water and dried in air at room temperature as well.

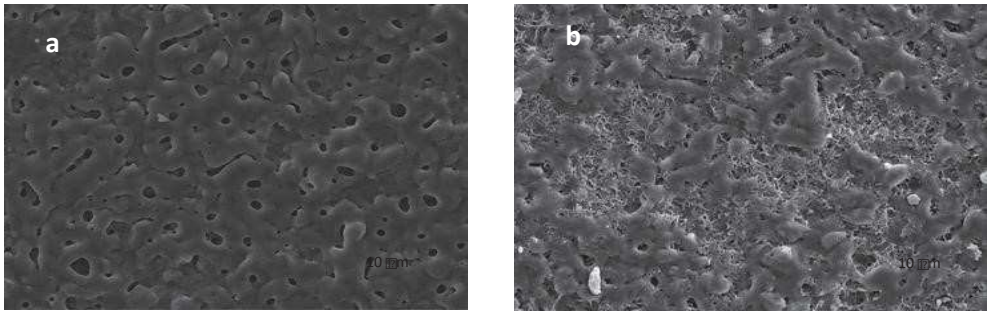

Figure 1– SEM micrographs of PEO sample (a) and PEO sample with LDH-NO_3 (b).

Fig. 1 shows plan view SEM micrographs of as prepared PEO (15 min 400 V) and PEO-LDH-NO_3 specimens. The PEO sample (**Fig. 1a**) shows the typical surface morphology of plasma electrolytic oxidation layers with pores and cracks at the discharge channel sites, due to the thermal stresses and gas evolution through the molten oxide material during the PEO process, respectively. Synthesis of LDH-NO_3 on the PEO coated AA2024 specimen leads to the coverage of the surface with a layer of flake-like microstructures (**Fig. 1b**).

The typical LDH flakes with size of about 1–2 μm can be clearly observed for PEO formed under 350 and 400 V. However, for higher voltages there is a significant decrease of the density of LDH flakes.

Schematically, Zn-Al LDH synthesis is based on the following chemical reactions:

$$Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2Al(OH)_4^- \quad (1)$$

$$Zn^{2+} + OH^- \rightarrow Zn(OH)^+ \quad (2)$$

$$Zn(OH)^+ + Al(OH)_4^- + NO_3^- + H_2O \rightarrow LDH\text{-}NO_3 \quad (3)$$

The LDH growth strongly depends on the dissolution of Al_2O_3 both from the bulk of the PEO coating (α-Al_2O_3 + amorphous Al_2O_3 in frame of this work) and/or amorphous Al_2O_3 from PEO layer.

The XRD patterns of the PEO specimens treated at different voltages show that PEO coatings formed under 350 V and 400 V have very strong peaks of Al from the substrate, a halo at low angle (related to amorphous phase) and gamma alumina peaks (**Fig. 2a**).

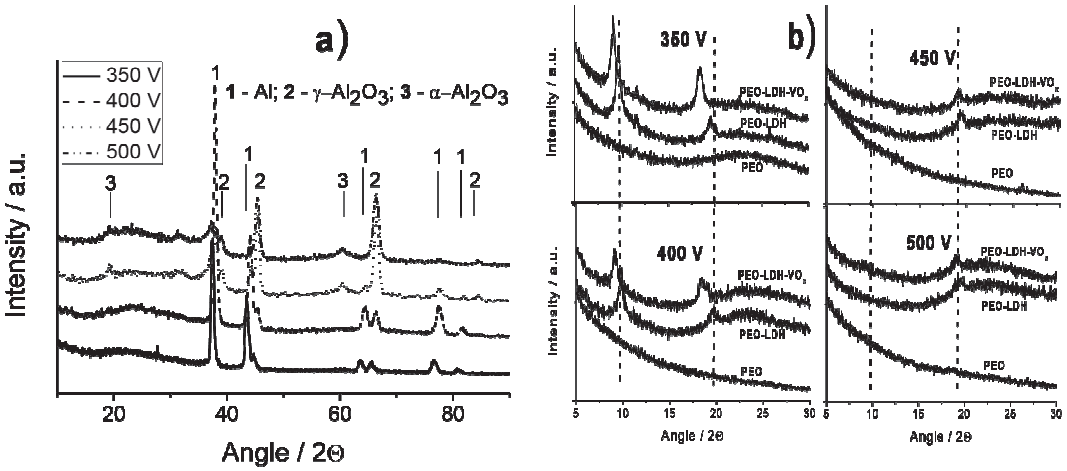

Figure 2 – XRD patterns of PEO coated AA2024 at different voltages (350 V-500 V) (a) and covered with LDH and inhibitor intercalation (LDH-VOx) (b).

For coatings formed at 450 V and 500 V alpha alumina peaks can be detected as well (**Fig. 2a**). This mixture of α-Al_2O_3, γ-Al_2O_3 is more stable and let it difficult to release $Al(OH)_4^-$ anions to form LDH flakes. As it can be seen from **Fig. 2b**, on respective XRD patterns at lower voltages (350 V and 400 V) well-defined peaks at 9.64° and 19.34° are detected and corresponds to the characteristic (003) and (006) reflections of LDHs. After the anion exchange reaction with vanadate, a shift can be observed in those peaks corresponding to the increase of intergallery distance and successful formation of LDH-VO_x.

Scanning vibrating electrode technique (SVET) was used in order to study the self-healing effect and validate the improvement of corrosion protection provided by formed PEO coatings with LDH post-treatment.

In a SVET system, vibrating tip (with diameter about 20 µm and amplitude of vibration about 30 µm) scans at 100 µm from the surface and detects anodic and cathodic corrosion currents in artificial micro-scale defects.

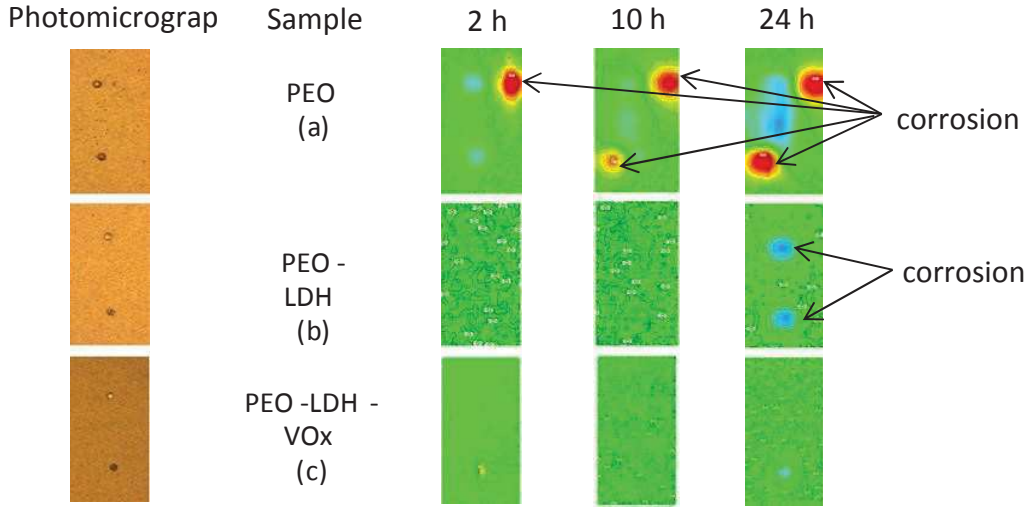

Figure 3 – Photomicrographs and SVET maps of PEO (a), PEO-LDH-NO_3 (b) and PEO-LDH-VO_x (c) after 2 h, 10 h and 24 h of immersion in 0.05 M NaCl

Fig. 3a shows that corrosion activities appeared not only at the places of artificial defects, but also at the other places, since PEO layer contains a lot of pores and defect. From **Fig. 3b** it is evident, that for sample PEO-LDH-NO_3 the detected activities are already significantly lower and detectable only after 24 hours of immersion. Sample PEO-LDHVO_x (**Fig. 3c**) shows the best corrosion behavior and almost no detectable corrosion during the time of immersion.

As a summary of this work, LDH-based sealing post-treatment for PEO covered AA2024 is reported. The amount of LDH flakes on the surface of PEO layers, decreased for higher voltages treatments. Formed LDHs were further loaded with corrosion inhibitor (vanadate) and tested for self-healing anti-corrosion properties. The obtained results clearly demonstrate that LDH functions as "smart" nanocontainers when loaded with anti-corrosion inhibitors and enhance the corrosion protection behavior.

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